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MODELING OF THE STRUCTURE OF POWDER SYSTEMS

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Analytical expressions are obtained for the bulk density of monodispersed powder systems, taking account of the properties of the particles. The structural and percolation approaches as well as taking account of the boundary layer thickness substantially simplify the evaluation of the properties of powder filled compositions. It is shown that the computed data are in good agreement with the experimental data.

Key words: powder systems, structure, particle size, density, modulus of elasticity.

Different structural and percolation models as well as different fractal methods are used to describe powder materials which are nonuniform on macroscopic and microscopic scales, specifically, ceramics [1–7].

To evaluate the properties of porous and composite mono- and bi-dispersed materials it is necessary to take account of the decrease of the bulk density of the filler V_r as the diameter of the particles decreases or the specific surface area increases, since it changes the characteristic of the system. For porous materials $V_r = 1 - P_r$ (P_r is the bulk porosity). We note that the standard volume concentration of free smooth spherical particles in bulk or their random packing density $V_{r0} = 1 - P_{r0}$ is 0.637.

Let the clusters (compact accumulations of particles) be spherical on average and let the order be different depending on the porosity of the system and in accordance with the fractal approach, i.e., the clusters can be the particles of a cluster system of a higher order. Likewise, let the small particles be distributed in the gaps between larger particles (or clusters of these particles) with random packing density V_r . In systems with elongated particles the relative bulk density V_r can be expressed as $V_r = 1.5 + (L/D)^{9/8}/11$, where D and L are, respectively, the diameter and length of the elongated particles [5].

In [5] a relation that gives a good fit to experimental data was proposed for bulk density of monodispersed systems:

$$\left. \begin{aligned} V_r &= 1 - 0.1 \left(\frac{0.001D}{D_0} \right)^{-0.19} \\ &\text{for } D_0 = 10^{-3} \text{ m} > D > 6.5 \times 10^{-6} \text{ m}; \\ V_r &= 0.63 \text{ for } D \geq 10^{-3} \text{ m}; \\ V_r &= 0.97 \text{ for } D \leq 6.5 \times 10^{-6} \text{ m}. \end{aligned} \right\} \quad (1)$$

Taking account of the shape and roughness of the particles according to the specific surface area of the particles $D = 6/S_0$ the expression (1) can be written in the form

$$\begin{aligned} V_r &= 1 - 0.1(6/S_0)^{-0.19} \\ &\text{for } 6000 \text{ m}^{-1} < S_0 < 9.23 \times 10^5 \text{ m}^{-1}; \\ V_r &= 0.63 \text{ for } S_0 \leq 6000 \text{ m}^{-1}; \\ V_r &= 0.97 \text{ for } S_0 \geq 9.23 \times 10^5 \text{ m}^{-1}. \end{aligned}$$

However, it is useful to obtain analytic relations for the bulk density of monodispersed system taking account of the properties of the particles.

For this we shall determine the content of the small and large particles in a bi-dispersed system with maximum density, i.e., as $D/D_0 \rightarrow 0$ the maximum relative packing density of the particles in the system $V_{\max} = 0.637 + 0.363 \times 0.637 = 0.868$. Then the large-particle fraction in unit volume of the material with maximum particle size is $C_{\text{size.max}} = 0.637/0.868 = 0.734$.

Let us evaluate the minimum ratio of the sizes (diameters) of the large and small articles or clusters under the condition that the small particles (clusters) fall between the large particles. In [4] it is established that for ordinary dispersed systems it is sufficient to consider three-layer clusters; then the distance between the center of a cluster to the center of the particles of the outer layer is $l = 1.82D$ (i.e. the average diameter D_{i+1} of the cluster formed is $2l_i = 3.64D_i$).

We assume that the degree of clusterization of the system increases with decreasing particle size (because of an increase of the interparticle interaction forces). According to the experimental data, for particles larger than 1 mm the degree of clusterization is zero and for dust particles (size close to zero) it can be regarded as maximum and equal to 0.734. This corresponds to the volume ratio of large and small phases in the highest density packing, studied above, of a

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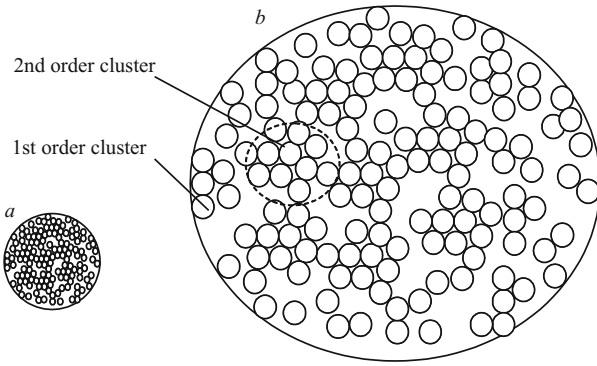


Fig. 1. Model of a two-dimensional cluster of first (a) and second (b) orders.

bi-dispersed system. Figure 1 shows a model of a two-dimensional (for clarity) cluster. It is evident that it is almost of a fractal character (i.e., as the scale increases, like but smaller elements of a similar structure appear).

Then the following expression can be written for the clusterization A of a monodispersed system of particles of clusters:

$$A = 0.734(1 - D/D_0) \text{ or } A = 0.734(1 - 6000/S_0). \quad (2)$$

By interpolation from the computational data of [5] we obtain for random monodispersed packing (average coordination number with bulk density $Z_r = 7.3$) a ratio of the intercluster to cluster porosity equal to 0.93. For this reason it can be assumed that with cluster formation the density of the clusters increases by $1/0.93$ and the intercluster density does not change.

It is convenient to start the analysis with the smallest first-order clusters and then analyze larger clusters — second-order and so on. In a system containing the smallest clusters of size D , we take account essentially only of its nonuniformity (ratio of the intercluster-to-cluster porosity). We have for the density of such a system

$$V_1 = 0.637[(1 - A) + A/0.93]. \quad (3)$$

For systems containing clusters of size D_1 and $D_2 = 3.64D_1 = 3.64^2D$, we take account of the intracluster porosity. The result is

$$V_2 = V_1[(1 - A) + AV_1/0.93].$$

We obtain a similar result for a system containing clusters of size D_1, D_2, \dots, D_i ($D_{n-i} = 0.001/3.64^i$):

$$V_i = V_{i-1}[(1 - A) + AV_{i-1}/0.93]; \quad (4)$$

$$\left. \begin{aligned} V_r = V_n = V_{n-1}[(1 - A) + AV_{n-1}/0.93] \\ \text{for } D_0 = 10^{-3} \text{ m} > D > 1.56 \times 10^{-6} \text{ m}; \\ V_r = 0.63 \text{ for } D \geq 10^{-3} \text{ m}; \\ V_r = 0.97 \text{ for } D \leq 1.56 \times 10^{-6} \text{ m}. \end{aligned} \right\} \quad (5)$$

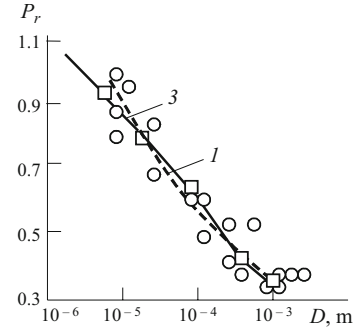


Fig. 2. Bulk density D_r of dispersed systems versus the average size D of the constituent particles: 1) fit of the function (1); 2) experimental data (\circ); 3) calculations using the expressions (2) – (5).

The reference values of the cluster sizes can be found from the relation $D_{n-i} = 0.001/(3.64^i)$: $D_n = D_0 = 0.001$ mm, $D_{n-1} = 0.000275$ mm, $D_{n-2} = 0.0000755$ mm, $D_{n-3} = 0.0000207$ mm, $D_{n-4} = 0.0000057$ mm. The lower limit of the particle size is $D_{\min} = 1.56 \times 10^{-6}$ mm, since calculations of V_r of the system give 0.0298, which corresponds to the maximum experimental values of the porosity of powder systems.

Computational Algorithm. We shall determine the required number of computational steps n ($2 \leq n \leq 6$) with the aid of the auxiliary value $n_{\text{aux}} = 1 + (1 - D/D_0)/3640$, rounding the value obtained to the next highest integer.

We calculate V_r with the required number of computational steps using the relations (2) – (5).

Figure 2 displays the bulk porosity of powder systems as calculated from the expressions (2) – (5). The figure also shows the experimental data and the fit of function (1). Evidently, the calculations based on the expressions (2) – (5) are in good agreement with the experimental data and the function (1). In contrast to the latter the proposed method reflects the particle sizes and the degree of clusterization as well as the fact that the intracluster porosity in the system is less than the intercluster porosity.

The large variance of the experimental data is explained by the use of particles with different shape and roughness. To refine the calculations the particle size can be taken as the value calculated according to the average specific surface area of the particles $D = 6/S_0$.

It is of interest to evaluate the fractal size of the cluster model described above. For a random system of spheres with random packing $V_r = 0.637$ and $D_n = 1$ we obtain

$$N_n = 6V_n/(3.14D_n^3);$$

where N_n is the number of clusters per unit volume of the materials with n computational steps; V_n is the relative packing density of particles in a system with n computational steps, $D_{n-i} = D_n/3.64 = 0.2747D_n$, with density 0.637 in the space between the spheres D_n and so forth. If one sphere

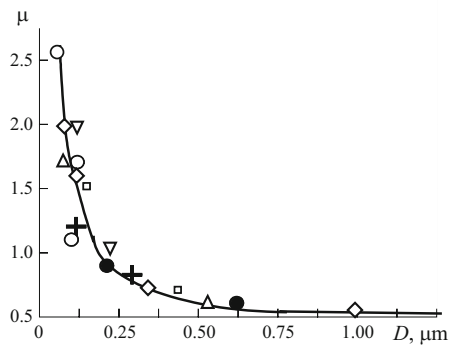


Fig. 3. Internal coefficient of friction μ of powders as a function of the average diameter of the particles according to the experimental data of [3]: \diamond) Al_2O_3 ; \bullet) Si_3N_4 ; \circ) ZrO_2 ; \triangle) MgO ; \square) Al(OH)_3 ; ∇) AlN ; $+$) TiN ; solid curve) according to the expressions (6).

($N_n = 1$) is used as the initial sphere, then according to the theory of fractals [6] we have

$$D_i = D_n Z^i = Z^n,$$

where Z is the order of the self-similar relation.

According to the Hausdorff – Besikovich relation taking account of the fact that $Z = 1/3.64$ and the number of particles (or lower-order clusters) in a cluster $p = 28$ [6], we obtain for the dimension d of a disperse system

$$d = \ln p / \ln (1/Z) = \ln 28 / \ln 3.64 = 2.58.$$

Therefore, the fractal character of the powder system is confirmed.

For systems with average particle size less than $6.5 \mu\text{m}$, where there is no correlation between the porosity and the average particle size in the system, it is convenient to use the internal coefficient of friction μ

$$\left. \begin{aligned} \mu &= 0.5 + 0.03(D - 6.5) \quad \text{for } 10^{-6} < D < 6.5 \times 10^{-6} \text{ m}; \\ \mu &= 1.4 + (1 - D)^4 \exp(1 - D) + 0.5165 \quad \text{for } D \leq 10^{-6} \text{ m}. \end{aligned} \right\} \quad (6)$$

Figure 3 shows the dependence of the internal friction coefficient on the average particle diameter according to the expressions (6) and the experimental data of [3]. It is evident that the computed and experimental data are in good agreement with one another.

When evaluating the properties of composite materials, aside from the decrease of the relative bulk density of the fill V_r with decreasing particle diameter, it is also necessary to take account of the higher mechanical properties of a polymer (boundary) layer with thickness h_f of the order of $0.15 \mu\text{m}$ adjoining the surface of the filler particles or the increase of the effective particle size by this thickness. As a result the effective volume concentration of the fill V_{eff} can be expressed as

$$V_{\text{eff}} = V_r (D + 2h_f)^3 / D^3, \quad (7)$$

where V is the relative density of the fill and D is the average (over the squared radius) size of the fill particles.

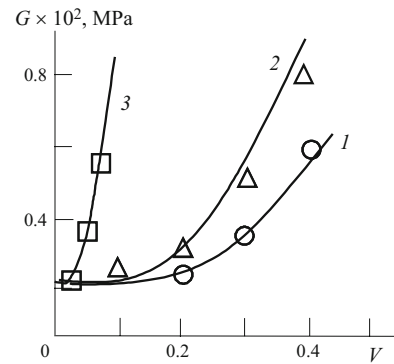


Fig. 4. Modulus of elasticity of filled polymer systems: 1) fraction 120 – 400 μm with bulk density 59.8% (quartz); 2) fraction 5 – 10 μm with bulk density 49.0% (quartz); 3) fraction 0.001 – 0.004 μm with bulk density 10.1% (aerosil-175); 1 – 3) calculation using the expressions (8) and (9); points) experimental data of [8].

When using instead of the experimental data on V the effective values of the concentration V_{eff} according to the expression (7) the experimentally determined threshold (critical) values V_{cr} will not contradict percolation theory, and then other structural characteristics and technological particulars of obtaining a polymer filled composite material can be analyzed.

We shall examine the percolation estimate of the modulus of elasticity of polymer systems with a filler based on silicon oxide (granite, quartz, aerosil), making it possible to take account of the effect of the filler density in a free-fill state V_r on its critical density V_{cr} [5]:

$$E = (E_0 - E_p) \left(\frac{V(D + d)^3 / D^3 - V_{\text{cr}}}{V_r(D + h)^3 / D^3 - V_{\text{cr}}} \right)^{1.8} + E_p, \quad (8)$$

where E , E_0 , and E_p are, respectively, the modulus of elasticity of the filled polymer, the filler powder with the bulk density, and the polymer; V_{cr} is the threshold density of monodispersed powder or fiber systems, which is related with the bulk density V_r by the following expression [5]:

$$V_{\text{cr}} = V_r^{1.8} / 2.82 + 0.003. \quad (9)$$

The expressions (8) and (9) with $E_{0(p)} = 1.1 \times 10^4$ (2.2×10^3) MPa determined from the data of [8] were used to calculate the modulus of elasticity of different fractions, filled with mineral components (quartz, granite, aerosol), with different density of the polymer systems (based on furfural acetone resin). The computational results are presented in Fig. 4. As one can see, the calculations are in good agreement with the data.

In summary, the structural and percolation approaches make it possible to simplify considerably the evaluation of the properties of powder systems and filled polymer composites. The packing ratios of the particles of the mineral fill and the thickness of the boundary layers must be taken into

account. The expressions (7) – (9) can be used, for example, to optimize the compositions and properties of composites containing an abrasive filler and powder binder consisting of glass in the fabrication of the ceramic abrasive articles.

The approach proposed here makes it possible to refine the modeling of the properties of porous powder materials.

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